STUDIES CONCERNING THE FIELD APPLICATIONS OF TELONE AND DD IN CALIFORNIA IN 1979 AND THE AMBIENT AIR CONCENTRATIONS OF THESE PESTICIDES DURING AND FOLLOWING APPLICATION BY SHANK INJECTION INTO SOIL IN FIELDS

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Division of Pest Management, Environmental
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SUMMARY

In 1979, a study was made of selected California fields in which either Telone or DD was injected into soil as a preplant nematicide with specially adapted equipment. These pesticides were injected into fallow fields approximately 8 inches deep at rates of 2 to 20 gallons per acre. The fields studied were being prepared for plantings of tomatoes, spinach, onions, or sugar beets. The time weighted average (TWA) for 1,3-dichloropropene, which is found in Telone and DD, has been set by the American Conference of Governmental Industrial Hygienists at 1 ppm. Air samples were collected in various locations at the application site. Air concentrations of Telone or DD in the tractor driver's breathing zone averaged about 380 ppb. With one exception, these levels did not exceed 1 ppm. During the loading of DD via a closed system, the highest exposure level reached outside the respirator was 3.9 ppm. The use of a respirator reduced the level from 356 ppb outside the mask to 14 ppb inside the mask during a transfer operation. The air concentration in the tractor driver's breathing zone is expected to be below 1 ppm, and no respirator should be necessary if either (1) the supply tanks are vented with tubing to a point behind the driver and near the shanks, (2) a positive pressure system is used to force the chemicals out of the supply tanks, or (3) the tanks are vented through charcoal filters. The average level of Telone or DD found midfield was 165 ppb at the time of application, 56 ppb 24 hours after application, and 37 ppb 48 hours after application. No midfield measurement exceeded 425 ppb, with most values below 100 ppb. Average levels of Telone or DD measured at the edge of the treated field (usually downwind) were 224 ppb at the time of application, 68 ppb 24 hours after application, and 34 ppb 48 hours after application. Levels of Telone or DD found 100 feet downwind from the treated field averaged 53 ppb at the time of application, 60 ppb 24 hours after application, and 58 ppb 48 hours after application. All samples were taken 4 feet above ground. With the exception of 4 fields, the 24-hour levels were below 100 ppb, and many of these were less than half of this level. The 48-hour levels showed further decrease from the 24-hour levels; the highest level found at 48 hours being 73 ppb. The air levels found in the field for 48 hours after application do not pose a safety hazard to persons who may enter the area.

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INTRODUCTION

Telone and DD are widely used pre-plant liquid nematicides. The primary toxic ingredient in these products is 1,3-dichloropropene (1,3-D). Telone is almost pure 1,3-D; and in DD, the major ingredient is 1,3-D, but it also contains significant amounts of 1,2-dichloropropane (1,2-D), 3,3-dichloropropene (3,3-D), and 2,3-dichloropropene (2,3-D). All of these ingredients are of similar toxicity.

There are acute toxicity hazards to be guarded against such as possible kidney damage from excessive inhalation and/or dermal exposure to 1,3-D. The chemical has been shown to be a mutagen by bacterial tests, but, to date, no animal studies have shown it to be a carcinogen. Dow Chemical Company, Shell Chemical Company, and the American Conference of Governmental Industrial Hygienists have recommended that a TWA of 1 ppm not be exceeded in the workplace, and that dermal exposure be kept to negligible levels. The Department tentatively accepts the 1 ppm TWA for the total amount of 1,3-D in Telone and 1 ppm for the total amount of 1,3-D, 1,2-D, 3,3-D, and 2,3-D in DD as acceptable exposure levels for 8-hour periods.

As a result of observations made in 1977, and in looking over data supplied by registrants, it became apparent that under certain circumstances, applicators of Telone and DD could be exposed to excessive levels (above 1 ppm) of these chemicals. It appeared that excessive levels in the applicator's breathing zone occurred particularly during (1) open pouring of the pesticide into the application vehicle tanks, (2) the presence of contaminated tools, wiping cloths, and clothing inside a closed tractor cab, and (3) the open venting of the supply tanks containing the pesticide on the tractor so that the volatile pesticide was released near the driver's seat. Permit conditions that addressed these issues went into effect in 1978. Particular attention was directed at requiring closed-system transfer during loading which was expected to reduce inhalation exposure during loading and also reduce spills onto the applicator's clothing, tools, and equipment. The other major change was directed at reduction of exposure of the applicator to fumes from the supply tanks. This was accomplished by (1) the use of positive pressure application systems, (2) the use of charcoal filters on the tank vents, or (3) the placing of piping and tubing from the tank vent with fumes exiting at a point below and behind the driver and near or into the shanks.

MATERIALS AND METHODS

Fresno and Monterey Counties were chosen as sites for most of the field studies because of the number of applications available. Most of the pre-plant applications took place in the fall after harvest and before the rains, or in early spring before planting.

All of the applications monitored were systems which used closed-system transfer of the pesticide from bulk tanks into tractor supply tanks. Each of the application systems studied either (1) had a positive pressure

injection system with no tank venting, (2) the venting was accomplished by piping and tubing from the tank vents to a point below and behind the driver near or into the shanks, or (3) venting of tanks through charcoal filters. Five front-mounted shank operationswere studied; the remainder of the applications were with rear-mounted shank injection equipment. The application rate varied between 2 and 20 gallons per acre according to the crop and nematode problem.

Air samples were collected using DuPont Model P-4000 and MSA Model S or G personnel air pumps. The air samples were collected for approximately two hours duration with charcoal tubes (SKC-West Lot 107 Category 226-09). Analysis of the charcoal tubes was performed by procedures outlined in Appendix 1. The sensitivity of the analytical method used to recover 1,3-D from charcoal tubes was 0.1 ppb.

Air pumps were attached to the tractor driver, collecting air in his breathing zone. In a few cases, an MSA Ultra-Twin GMP full-face respirator, approval No. TC-23C-148, with approved organic cartridges with an inside sampling port was used to test the efficiency of respirator protection during application.

Air samples were also collected at midfield, edge of field, and downwind 100 feet during the application; and 24 hours and 48 hours following the application. Samples were collected 4 feet above the ground. All samples were labeled and transported on ice until it reached the laboratory for analysis.

RESULTS

The data accumulated is provided in Table 1.

DISCUSSION

The highest level of exposure to Telone or DD occurred during the loading process. The exposure was greatly reduced, however, by the use of a respirator.

The average level of Telone or DD in the tractor driver's breathing zone outside the respirator during application was approximately 380 ppb, with only one measurement exceeding the 1 ppm proposed TWA.

There was no substantial difference in the concentrations of Telone or DD found at midfield and at the downwind edge of the treated field. The average values at the time of application were 165 ppb and 224 ppb respectively. Most values found were below 500 ppb. Air concentrations at these sites were much lower 24 and 48 hours after application, with most levels below 100 ppb. Levels of Telone or DD found 100 feet downwind averaged 53 ppb at the time of application with no significant change occurring at 24 and 48 hours after application.

Possible clothing or skin contamination was not measured in this study. Levels of these chemicals in topsoil were not measured in this study.

CONCLUSIONS

Proposed Regulations

Based upon previous observations and data accumulated in this study, a set of permit conditions and proposed regulations was developed for the use of 1,3-dichloropropene (Telone/DD) in California. These are as follows:

1,3-dichloropropene. The use of 1,3-dichloropropene (Telone/DD) for soil treatment shall be made only in accordance with the following restrictions:

1. A closed system shall be used for all loading and transfer operations conducted by an employee.

2. Soap, at least 1 gallon of clean water, and an eye wash bottle full of clean water shall be available on the application vehicle.

3. Clean outer clothing shall be worn daily.

4. Employees who will use 1,3-dichloropropene shall be informed that overexposure may cause kidney damage.

5. Protective clothing (including boots and gloves) and a respirator approved for organic vapors shall be worn during mixing, loading, transferring, calibrating, repairing, cleanup of small spills, and/or when working in poorly ventilated areas. Protective clothing shall be either 1 mil or greater in thickness, and shall be made of polyethylene, rubber, nitrile, neoprene, or a material certified by the manufacturer to be impervious to undiluted formulations of these pesticides for at least 60 minutes.

    a. If protective clothing is 1 mil in thickness, it shall be disposed of immediately after contamination or one day's use, whichever occurs first.

    b. If protective clothing is 3 mil or greater in thickness, it shall be clean at the start of each day's use and, if contaminated, shall be immediately washed with soap and water, and air-dried outdoors.

    c. Protective clothing having the odor of these pesticides shall not be worn.

6. Employees applying 1,3-dichloropropene shall wear a respirator approved for organic vapors unless all of the following conditions exist:

    a. Soil injection shanks are mounted behind the driver;

    b. Rocks, large dirt clods, or trash do not interfere with proper soil incorporation; and

c. Tanks holding 1,3-dichloropropene, if vented, are vented through charcoal filters which are changed daily, or are vented through tubes that convey fumes to a point below and behind the driver near or into the shanks.

7. For 3 days subsequent to application, any employee entering fields treated with these pesticides shall wear boots and a respirator as specified in subsection 5.

Additional Observations Since Regulations Drafted

From the most recent data developed, it appears that the use of closed-system loading has so reduced loader exposures that a half-face respirator with organic vapor cartridges gives adequate worker protection during field loading. These studies have also confirmed that if the venting from applicator vehicle tanks is controlled as recommended, the tractor driver does not need to wear a respirator during the application process.

A comparison of levels of Telone and DD in the driver's breathing zone between front-and rear-mounted shanks did not show any significant differences.

It appears that the only reentry hazard is exposure to unprotected feet for 3 days subsequent to application, especially if the soil is wet. It is probable that the wearing of a respirator during reentry during the first 3 days after application is not necessary.

It is recommended that these more recent observations be taken into account in the final development of regulations and label statements.

TABLE 1

Amounts of Telone and DD found in the air during field applications in California in 1979. In the case of Telone, 1,3-dichloropropene was measured and reported in ppb as such. In the case of DD, both isomers of 1,3-dichloropropene were measured and the ppb figure reported assumed that the amounts of the other propenes and propanes in the air were in the same ratio as they occur in the formulation; thus the ppb figure reported for DD includes all of the propenes and the propanes.

Sample Date	Telone/DD Amounts (ppb)	Application Rate (gal/acre)	Product Used	Air Temperature °F	County	Location of Air Samples	Other Pertinent Data That Applies to Entire Study
			First Study				
4-13-79	356	-	DD	80	Yolo	15-20 ft. Downwind On Truck Hood During Loading	Preplant Tomato
4-13-79	14	-	DD	80		Inside Respirator During Loading	
4-13-79	1	-	DD	83		Inside Respirator During Application	
4-13-79	3	-	DD	83		Outside Respirator Driver Breathing Zone	
4-13-79	14	-	DD	83		Edge of Field Downwind	Tanks Vented Near Shanks
			Second Study				
5-01-79	392	-	Shell DD	71	Solano	Midfield	Preplant Sugar Beets
5-01-79	58	-	Shell DD	71		Breathing Zone On Tractor	
5-01-79	225	-	Shell DD	71		In Vehicle At Edge of Field	Tanks Vented Near Shanks
			Third Study				
5-23-79	629	5	Telone II	65	Monterey	In Cab of Tractor	Shanks in Front Positive Air Pressure System on Tanks
5-23-79	234	5	Telone II	65		In Field 4 ft. Above Ground	
5-24-79	11	5	Telone II	65		In Field 4 ft. Above Ground 24 Hour Later	
5-14-79	4	5	Telone II	65		Edge of Field 10 ft. Away 4 ft. Above Ground 24 Hour Later	
			Fourth Study				
5-24-79	0.1	5	Telone II	78	Monterey	In Closed Cab of Tractor	Shanks Mounted in the Front Positive Air Pressure System Used
5-24-79	75	5	Telone II	77		Midfield	
			Fifth Study				
6-20-79	479	12	Shell DD	68	Monterey	Outside of Tractor Cab	Spinach Preplant Closed Cab Shanks Mounted On The Front Venting to the Rear Air Conditioner On
6-20-79	424	12	Shell DD	68		Inside Tractor Cab In Driver's Breathing Zone	

TABLE 1 (Cont.)

Sample Date	Telone/DD Amounts (ppb)	Application Rate (gal/acre)	Product Used	Air Temperature °F	County	Location of Air Samples	Other Pertinent Data That Applies to Entire Study
				Sixth Study			
6-20-79	48	7	Shell DD	68	Monterey	Driver's Breathing Zone Inside Cab	Closed Cab Air Conditioner on Shanks in Front of Tractor Tank Vented To The Rear
6-20-79	728	7	Shell DD	71		Outside Cab Driver's Breathing Zone	
				Seventh Study			
7-10-79	145	8	Telone II	96	Kings	Driver's Breathing Zone	Preplant on Seed Potatoes Open Cab Shanks On The Rear Tank in Front and Vented to the Rear
7-11-79	61	8	Telone II	86		Driver's Breathing Zone	
7-11-79	149	8	Telone II	80		Edge of Field	
				Eighth Study			
8-08-79	71	-	Telone II	61	Monterey	Northeast Edge of Field; Wind from South	Front Mounted Shanks Tank in Rear And Vented to Rear
8-08-79	577	-	Telone II	60		Driver's Breathing Zone Inside Cab	
8-08-79	773	-	Telone II	60		Outside Tractor	
8-08-79	66	-	Telone II	60		Midfield	
				Ninth Study			
8-08-79	41	-	Shell DD	77	Monterey	Midfield 24 Hours After Application	
				Tenth Study			
8-9-79	93	-	Telone II	73	Monterey	Midfield 24 Hours After Application	
				Eleventh Study			
8-22-79	525	2	Terr-O-Cide-15-D	83	Los Angeles	In Breathing Zone of Tractor Driver Following Application Rig	Onion Preplant Tanks Vented To Rear
8-22-79	412	2	Terr-O-Cide-15-D	83		Midfield During Application	
8-22-79	421	2	Terr-O-Cide-15-D	83		In Breathing Zone of Tractor Driver at time of application	
8-22-79	145	2	Terr-O-Cide-15-D	83		Downwind; During Application	
				Twelveth Study			
10-2-79	127	15	Western Farm Service DD	88	Fresno	Midfield Immediately After Application	Preplant Tomatoes Field study after application
10-2-79	20	15	Western Farm Service DD	88		Downwind 100' Immediately After Application	
10-2-79	85	15	Western Farm Service DD	88		Edge of Field, Downwind, Immediately After Application	
10-3-79	25	15	Western Farm Service DD	88		Midfield 24 Hours Later	

TABLE 1 (Cont.)

Sample Date	Telone/DD Amounts (ppb)	Application Rate (gal/acre)	Product Used	Air Temperature °F	County	Location of Air Samples	Other Pertinent Data That Applies to Entire Study
10-3-79	19	15	Western Farm Service DD	82	Fresno	Downwind 100' 24 Hours Later	
10-3-79	16	15	Western Farm Service DD	82		Edge of Field 24 Hours Later	
10-4-79	10	15	Western Farm Service DD	84		Midfield 48 Hours Later	
10-4-79	8	15	Western Farm Service DD	84		Edge of Field 48 Hours Later	
			Thirteenth Study				
10-2-79	86	20	Telone II	91	Fresno	Midfield 1 Hour After Application	Preplant Tomatoes
10-2-79	247	20	Telone II	91		Edge of Field 1 Hour After Application	Field Study after Application
10-3-79	135	20	Telone II	86		Midfield 24 Hours Later	
10-3-79	204	20	Telone II	86		Edge of Field, Downwind, 24 Hours Later	
10-3-79	116	20	Telone II	86		Downwind 100' 24 Hours Later	
10-4-79	61	20	Telone II	88		Midfield 48 Hours Later	
10-4-79	47	20	Telone II	88		Edge of Field, Downwind, 48 Hours Later	
10-4-79	73	20	Telone II	88		Downwind 100' 48 Hours Later	
			Fourteenth Study				
10-3-79	1,824	9	Western Farm Service DD	86	Fresno	Driver's Breathing Zone At Time of Application	Shanks to the Rear Tank Vented to the Rear
10-3-79	48	9	Western Farm Service DD	86		Edge of Field; Downwind During Application	Tractor Cab Open
10-4-79	756	9	Western Farm Service DD	87		Driver's Breathing Zone at time of Application	
10-4-79	65	9	Western Farm Service DD	87		Edge of Field During Application	
10-4-79	3,932	9	Western Farm Service DD	87		Driver's Breathing Zone; During Loading Process	
10-5-79	34	9	Western Farm Service DD	79		Midfield 24 Hours Later	
10-5-79	40	9	Western Farm Service DD	79		Edge of Field 24 Hours Later	
			Fifteenth Study				
10-5-79	410	9	Western Farm Service DD	79	Fresno	Driver's Breathing Zone at Time of Application	Tractor Cab Open Shanks to the Rear Tank Vented to the Rear and to the Ground
10-5-79	33	9	Western Farm Service DD	79		Edge of Field Downwind During Application	
10-5-79	41	9	Western Farm Service DD	79		Midfield During Application	

TABLE 1 (Cont.)

Sample Date	Telone/DD Amounts (ppb)	Application Rate (gal/acre)	Product Used	Air Temperature °F	County	Location of Air Samples	Other Pertinent Data That Applies to Entire Study
			Sixteenth Study				
10-15-79	291	16	Shell DD	81	Fresno	Driver's Breathing Zone; During Application.	Preplant Tomatoes
10-15-79	1,008.2	16	Shell DD	81		Edge of Field During application, where the lines had been bled.	Shanks Were to the Rear
10-16-79	54.6	16	Shell DD	81		Midfield 24 Hours later	Tank Vented to the Rear
10-16-79	135.6	16	Shell DD	81		Edge of Field Downwind 24 Hours later	
10-17-79	42.6	16	Shell DD	83		Midfield 48 Hours later	Shank-Injected 12 Inches Deep
10-17-79	47.1	16	Shell DD	83		Edge of Field 48 Hours later	
			Seventeenth Study				
10-15-79	295.9	13	Shell DD	83	Fresno	Driver's Breathing Zone; inside closed cab with air conditioning on during application	Preplant Tomatoes
10-15-79	497.8	13	Shell DD	83		Outside of Cab During Application	Tank Vented to The Rear and to the Ground
10-16-79	ND	13	Shell DD	83		Edge of Field During Application	Shanks to the Rear
10-16-79	63.1	13	Shell DD	81		Midfield 24 Hours later	
10-17-79	36.3	13	Shell DD	88		Midfield 48 Hours later	
10-17-79	29.5	13	Shell DD	88		Edge of Field 48 Hours later	
			Eighteenth Study				
10-16-79	110.4	16	Shell DD	81	Fresno	Driver's Breathing Zone	Preplant Tomatoes
10-16-79	192	16	Shell DD	81		Edge of Field, Downwind, During Application	Tank Vented To The Rear Open Cab Shanks on the Rear
10-17-79	55.6	16	Shell DD	83		Midfield 24 Hours later	Shank-Injected 12" Deep
10-17-79	42.3	16	Shell DD	83		Downwind 100' 24 Hours later	
10-17-79	59.0	16	Shell DD	83		Edge of Field, Downwind, 24 Hours later	
10-18-79	38	16	Shell DD	75		Midfield 48 Hours later	
10-18-79	33.3	16	Shell DD	75		Edge of Field 48 Hours later	
			Nineteenth Study				
10-16-79	574.2	13	Shell DD	81	Fresno	Driver's Breathing Zone; Inside Closed Cab With Air Conditioning on.	Preplant Tomatoes Tank Vented to the Rear and to the Ground
10-16-79	617	13	Shell DD	81		Outside Cab This air measurement and the oen above Included a 10 Min. Transfer Operation With a Closed System	

TABLE 1 (Cont.)

Sample Date	Telone/DD Amounts (ppb)	Application Rate (gal/acre)	Product Used	Air Temperature °F	County	Location of Air Samples	Other Pertinent Data
10-16-79	25.4	13	Shell DD	81		Edge of Field, Downwind During Application	Shanks To The Rear
10-17-79	47.8	13	Shell DD	88		Midfield 24 Hours later	
10-17-79	52.8	13	Shell DD	88		Edge of Field, Downwind 24 Hours later	
10-17-79	61.1	13	Shell DD	88		Downwind 100' 24 Hours later	
10-18-79	36	13	Shell DD	79		Midfield 48 Hour	
10-18-79	32.5	13	Shell DD	79		Edge Of Field, Downwind 48 Hours later	

APPENDIX I

Original Date 3-2-79
Supersedes New

DETERMINATION OF TELONE II ON CHARCOAL TUBES

Scope:

This method is for the desorption and analysis of Telone II from charcoal air sampling tubes. It is intended solely for the use of the California Department of Food and Agriculture, Chemistry Laboratory Services.

Principle:

Telone II that has been collected from the air onto activated charcoal is desorbed from the charcoal with ethyl acetate, diluted as needed and analytically determined by gas chromatography using electron capture detection.

Reagents and Equipment:

1. Ethyl Acetate, nanograde.
2. Analytical Grade Telone II -- 1,3-dichloropropene.
3. Approved and calibrated personal sampling pump.
4. Charcoal tubes -- SKC #226-09.
5. Developing vials with teflon liners -- SKC #226-02.
6. Assorted microsyringes for preparing standards and gas chromatography.
7. Assorted pipets.
8. Volumetric flasks.
9. Small triangular file for scoring glass tubes.

Analysis:

Interferences: High humidity may affect trapping efficiency.

1. Score each charcoal tube with a file in front of the first section of charcoal.
2. Break open the tube. Remove and discard the glass wool.
3. Transfer the charcoal in the upstream section to a labeled desorption vial, and add a known amount of nanograde ethyl acetate. 2-4 ml is suggested.
4. Remove and discard the foam partition from the tube.
5. Transfer the second section of charcoal to a second labeled desorption vial, and add a known amount of nanograde ethyl acetate.
6. Allow the sample to desorb for 1 hour on the rotator.
7. Transfer an aliquot to a sample storage vial, label, and freeze until analysis time.
8. Determine by GLC.

Determination of Desorption Efficiency:

1. Remove the foam and second section of charcoal from a charcoal tube of the same lot number used for the determinations.
2. Inject a known amount of Telone II (1 to several hundred micrograms) into the charcoal with a syringe and cap the tube with the supplied caps.

3. At least five tubes (preferably at levels covering the expected range) should be prepared in this manner and allowed to stand at least overnight to assure complete absorption. A blank tube should be treated the same way except that no sample is added.
4. Analyze the tubes by the analytical procedure.
5. Desorption efficiency = $\frac{\text{Response sample-response blank}}{\text{Response standard}}$

   The standard is the same amount as injected into the charcoal tubes.

Calculations:

1. Determine weight of Telone II present on charcoal tube sections by GLC analysis. Nanograms or micrograms are most convenient.
2. Correct this total weight of Telone II by subtracting any blank value present on the blank tube.
3. The corrected weight is divided by the desorption efficiency to obtain the final weight of Telone II present.
4. The volume of air sampled is converted to standard conditions of 25°C and 760 mm Hg.

$$VS = V \times \frac{P \times 298}{760 \times (T+273)}$$

Where VS = Volume of air at standard conditions.
V = Volume of air as measured.
P = Barometric pressure in mm Hg.
T = Temperature of air in °C.

5. Calculate ppb in air from the above data.

$$\text{ppb (volume basis)} = \frac{ng \times 24.45}{VS \times 111.0} = \frac{ng}{VS} \times 0.2203$$

24.45 is the mole volume of Telone II at 25° and 760 mm.
111.0 is the molecular weight of Telone II.

Gas Chromatographic Conditions:

Gas Chromatograph with Ni^{63} or H^3 detector
Temperatures-Injector: 125°C
Detector: Follow manufacturer's suggestions

Column: 20' x 1/8" O.D. nickel tubing
10% SP-2100 on 100/120 Chromosorb W-HP
80° C, 25 ml/min N_2 carrier gas
Telone II retention time approximately 3.2 and 3.7 minutes

Column: 6' x 2 mm I.D. glass
80/100 Poropak Q
190°C, 30 ml/min N_2 carrier gas
EDB retention time approximately 9.5 minutes
Telone II retention time approximately 6 and 7 minutes

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